An International Butyltin Measurement Methods Intercomparison: Sample Preparation and Results of Analyses

W. R. Blair, G. J. Olson, F. E. Brinckman

U.S. DEPARTMENT OF COMMERCE
National Bureau of Standards
Institute for Materials Science and Engineering
Ceramics Division
Surface Chemistry and Bioprocesses Group
Gaithersburg, MD 20899

R. C. Paule

National Measurement Laboratory
National Bureau of Standards
Gaithersburg, MD 20899

and

D. A. Becker

Nuclear Methods Group
National Bureau of Standards
Gaithersburg, MD 20899

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AN INTERNATIONAL BUTYLTIN MEASUREMENT METHODS INTERCOMPARISON: SAMPLE PREPARATION AND RESULTS OF ANALYSES

W. R. Blair[1], G. J. Olson[1], F. E. Brinckman[1], R. C. Paule[2] and D. A. Becker[3]

[1]Surface Chemistry and Bioprocesses Group, National Bureau of Standards

[2]National Measurement Laboratory, National Bureau of Standards

[3]Nuclear Methods Group, National Bureau of Standards

Abstract

A comparison of organotin measurement methods has been conducted with a new tributyltin research sample distributed to over 40 laboratories worldwide. A description of background research into the behavior and manipulation of low concentration aqueous organotin solutions, chromatographic production of the speciated aqueous organotin research material, and quantitative results from the methods intercomparison are reported here along with recommendations for future work.

Keywords: chemical speciation; liquid chromatography; methods intercomparison; molecular characterization; round-robin; research material; stability; tributyltin; ultratrace organotin solutions

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Certain trade names and company products are mentioned for identification purposes only and in no case does it imply recommendation or endorsement by the National Bureau of Standards.

1.0 Introduction

Worldwide production of organotin chemicals has increased significantly over the past 30 years, to a present level of more than 35,000 tons annually (1). Numerous applications as catalysts, polymer stabilizers, and tailored biocides have resulted from the highly varied chemical and biological properties provided by different classes of organotin(IV) compounds. For example, some recent studies (2,3) have quantitatively correlated the number, size, and shape of organic moieties bound to tin with physicochemical and toxic properties of the molecule, with triorganotins displaying greatest effects towards most organisms. The mono- and di- organotins, $RSnX_3$ and R_2SnX_2, are widely employed as heat and light stabilizers in the PVC plastics industry (4) and as catalysts for silicones and polyurethane foams (5). The highly selective biocidal properties of triorganotin compounds, R_3SnX, chiefly dependent upon the kind of tin-bound organic groups, have resulted in their wide use as the active ingredient in wood preservatives, antifouling paints, fungicides, and miticides (6-9). Among the organic groups proven in laboratory and extensive field testing to be most generally effective as preservatives, antifoulants, and fungicides, the tri-n-butyltin moiety has received greatest commercial impetus (10), and it is with this class that significant commercial growth is anticipated. Tetraorganotins, R_4Sn, have no large industrial outlets, but are used mainly as intermediates in the manufacture of other organotin compounds (1,11).

As the use of organotins has increased, international scrutiny of the fate and effect of these compounds in the environment has also increased. These concerns are reflected in environmental assessments and pollution evaluations compiled by industry (12) and national environmental agencies of several countries (13-15), including the United States Navy (16). For example, in a situation where aquated tributyltin ion is toxic to some sensitive aquatic organisms at µg/L (ppb) levels (17), and the dibutyltin compound is comparatively nontoxic (3), it is essential that monitoring methods yield chemical speciation data for all the active organotins present in an environmental sample in order to provide a rational, equitable and effective basis for regulation. Numerous methods for the determination of total tin are described in analytical literature (13,18), but unfortunately, the bulk of these methods are inapplicable to isolation, separation, and quantitation of organotins in environmental media at relevant ppb action levels.

1.1 Current Status of Organotin Measurements

Within the past several years many new methods have been described which provide the required trace organotin speciation information. Examples are summarized in Table 1 (Table 1 adapted from: The Occurrence and Pathways of Organometallic Compounds in the Environment-General Considerations, P. Craig and F. E. Brinckman, in The Environmental Chemistry of Organometals, P. Craig, Ed., Longmans-Green, London, 1985) which illustrate the basic steps of analyte preconcentration. In general, most of these methods rely on two-phase solvent extraction of the organotins from the environmental sample, concentration and often derivatization by sodium

borohydride or Grignard reagents before chromatographic or boiling point separation with tin determination by a tin-selective (flame photometric) (19) or tin-specific (atomic absorption) detector (20). With the availability of analytical techniques possessing the requisite speciation and detection level capabilities, reports began to appear concerning the environmental distribution of organotins, revealing a globally dispersed baseline concentration of methyltins at the ng/L level in aquatic systems (21). Since methyltins are not commercially produced in major amounts, the pathway for their formation could involve both biological (22) and abiotic (23,24) methylation of inorganic tin or biodegradation of the man-made organotins discussed above (25,26). The need to elucidate further the biogeochemical cycles of tin is reinforced by the development and rapidly emerging use, on a worldwide basis, of tri-n-butyltin-containing marine antifoulant coatings. Although the potential for food chain accumulation of tributyltin via a marine microbial pathway has been reported (27) very little else is known about the environmental persistence, degradation rates, and possible accumulation sites of tributyltin, though recent unpublished reports suggest an environmental half-life of less than two weeks in certain samples of marine and estuarine waters (G. J. Olson, unpublished results; P. Seligman and R. Lee, personal communication).

1.2 Basis and Scope of an Organotin Measurement Methods Intercomparison

Anticipating the need of reference standards for calibration and intercomparison of current and future organotin analytical methods, the National Bureau of Standards, with support of the Office of Naval Research, initiated a program to evaluate the factors essential to conducting an

interlaboratory measurement methods comparison for organotins. Among the chief parameters to be assessed were:

(a) Choice of most significant and representative organotin analyte and matrix suitable for diverse participants and analytical state of art;

(b) Evaluation of contact materials and mode of preparation, storage, and transport of candidate interlaboratory organotin research materials;

(c) Concurrent with, and in support of, (a) and (b), elucidation of the appropriate solution chemistry and mode(s) of preparation of a stable organotin analyte affording sufficient shelf life for present and future intercomparisons, and ultimately assuring a means for certified reference materials preparation (28).

(d) Merging successful features of (a), (b), and (c) in an inaugural intercomparison protocol suited to international participation and uncomplicated sample delivery and reportage.

1.3 Organization of the Organotin Intercomparison Study

Frequent contacts with colleagues, collaborators, and our NBS sponsors over recent years made clear the marked preference for an initial comparison of various methods for the quantitation of the tributyltin cation species, especially in aqueous medium, irrespective of geganions. Not only was selection of this prospective analyte consistent with the bulk of most recent analytical literature (Table 1), this biocidal species has received the greatest attention among environmentalists and regulatory bodies in the homelands of all of the proposed participants. For some years, our laboratory has dealt with trace organotins, including tri-n-butyltin, and this familiarity with the manipulative difficulties of organotins provided

an opportunity to assess closely questions of contact and container materials, solution stability and effects of light, impurities, and chemical forms. Moreover, our experience with trace chemical speciation studies of a variety of neutral and ionic organotins based upon liquid chromatographic separation schemes (29), lent credence to successful development of a tri-n-butyltin solution of high purity suited to the stringent requirements of an intercomparison study.

1.4 Development of the Experimental Plan

Prior to design of the organotin sample generation apparatus or selection of a sample container, the effects of four container materials on the stability of low concentration aqueous solutions of tri-n-butyltin were evaluated. The containers were commercially available bottles (125 to 250 mL) made of borosilicate glass (Pyrex), polytetrafluoroethylene (Teflon), polycarbonate, and conventional polyethylene. Deionized water was chosen as the sample solvent because our earlier studies suggested its suitability as a universal medium for both neutral and ionic organotin compounds at low concentrations, e.g., ppm (1 mg/L) or less, which was the target concentration of an intercomparison material. Moreover, choice of water provided a safe and transportable, non-toxic, non-flammable medium suitable for easy dilutions by participants or other later users directly into freshwater and marine samples acquired from the field, thereby permitting methods of additions assessments. Finally, previous evidence from our laboratory for both analytical- and preparative-scale quantitative separations by aqueous ion-exchange liquid chromatography of organotins

suggested (29) a reliable method for producing pure tri-n-butyltin in water at ppm levels in quantities sufficient for a major round-robin protocol.

All of these design and production factors were consistent with the primary goal of the project: to cheaply and reproducibly produce and disseminate ample-sized packages of a relevant organotin in an appropriate solvent at some stable concentration. This allows round-robin participants the flexibility to dilute the sample in ways consistent with their own techniques but not compromising either quantification or chemical speciation analyses over extended periods of time.

2.0 Experimental

Specific details of the tin-specific quantitative analyses of aqueous solutions of inorganic and organotins, including butyltins, employing graphite furnace atomic absorption spectrophotometry (GFAA) have been reported in several recent papers (29-32).

2.1 Chemicals and Materials

The tin compounds used in this work were purchased commercially and used as received, with the exception of the bis(tributyltin)oxide (Alfa Products, Danvers, MA 01923) used in preparation of the research material, which was purified by vacuum (0.01 Torr) distillation just prior to use. All laboratory glassware used for preparation, storage, and dilution of stock organotin solutions and the various storage bottles used in this work were cleaned prior to use by leaching for 24 to 48 hours with dilute aqueous nitric acid (5 to 10%). When container size allowed, the acid-filled bottles and glassware were placed in a warm water bath

(approximately at 40° C) during leaching. After leaching, all items were rinsed 4 to 5 times with deionized water of 15 to 18 megaohm cm^{-1} resistance (Aqua Suma 36, Culligan Water Conditioning, Vienna, VA 22180).

2.2 Organotin Analytical Procedures for Aqueous Media

The methods described below emphasize marine or saline media, which represent difficult matrices in environmental analyses, but are also applicable to fresh water samples.

2.2.1 Total Tin Determination by Graphite-Furnace Atomic-Absorption Spectroscopy (GFAA)

A sensitive method for determination of the levels of total extractable organotin compounds present in aqueous saline samples has been developed at NBS and is described in detail in a separate publication (30). Basically, the method recommends preconcentration of the organotin compounds in a sample by extraction into toluene, followed by determination of total tin concentration by graphite furnace atomic absorption (GFAA) spectroscopy. Both the sensitivity and element specificity needed to determine nanogram quantities of tin are provided by GFAA, but sensitivity suffers significant losses when the sample matrix contains salts. For this reason, the toluene extract must be washed several times with deionized water prior to GFAA analysis.

Enhancement of GFAA sensitivity can be achieved by physical, chemical, or combined methods. Physical enhancement involves inserting graphite platforms, referred to as L'vov platforms (33) into the conventional furnace tube. Analyte volatilization is delayed by the elevated platform, which

reaches maximum temperature more slowly than the furnace tube itself, thereby reducing the probability that analyte will be volatilized before the absorption signal is measured. The L'vov platform thus provides a physical means of signal enhancement for a number of elements. Additionally, we have discovered a chemical matrix modification technique employing transition metal oxo-salts that specifically provide signal enhancement for tributyltin compounds (34).

2.2.2 Molecular Tin Quantitation

Determining the molecular species of organotins present in saline aqueous samples is routinely done at NBS by simultaneously hydridizing the sample with sodium borohydride while extracting with dichloromethane (35,36). The dichloromethane extract is injected into a gas chromatograph equipped with a flame photometric detector for identification of the organotins present. For a typical analysis of saline water with butyltin concentrations in the sub-µg/L range (as tin), the following procedure has been developed. To a 100-mL of sample in a 125-mL glass separatory funnel equipped with a Teflon stopcock and Teflon-lined screw cap, add 2.8 mL dichloromethane and 2.0 mL of 4% (w/v) aqueous $NaBH_4$. A 10 µL spike of 0.5 µg/mL aqueous solution of di-n-propyltin dichloride can be added to the sample to serve as an internal calibrant. The funnel is then capped, shaken by hand for 15 to 30 seconds, vented and then shaken (240 strokes/min) on a wrist action shaker for 10 min. Following a 5 min. settling period, the bottom organic layer is removed. An additional 1.4 mL of dichloromethane is added and the 10 min. extraction repeated. The organic layers are combined in small (approx. 2 mL volume) polypropylene

centrifuge tubes and the solvent volume reduced to 100 to 500 µL by evaporation with a gentle stream of air. Appropriate blanks are carried through the same procedure. While most of our work has been done with samples of 100 mL volume, samples of 800 to 1000 mL have been analyzed using 1 liter separatory funnels and proportionately larger volumes of all reagents. Sensitivity when using 100 mL samples is approximately 7 ng Sn/L for tetrabutyltin and tri-n-butyltin, 3 ng Sn/L for dibutyltin and 22 ng Sn/L for mono-n-butyltin.

2.3 Stability of Dilute Aqueous Tri-n-Butyltin Solutions in Various Container Materials

A series of 125 mL and 250 mL screw-capped bottles, typical of those employed in most analytical laboratories were chosen for evaluating both short- and long-term effects of various container materials on dilute aqueous tri-n-butyltin solutions. In addition to considerations of chemical effects by wetted materials, surface-to-volume, leakage, resistance to impact, and cost played important roles in selection of test containers, purchased from a number of commercial suppliers.

Four different commercial container materials were used in the study: Pyrex glass; Teflon; polycarbonate; and conventional ("low-density") polyethylene. One bottle of each material was filled with a freshly prepared stock solution of 30 ppb (30 µg/L as Sn) of either stannous chloride, $SnCl_2$, or tri-n-butyltin chloride in deionized water. This concentration range was selected as that representing the convenient measurement range for analytical methods either providing total tin or molecular tin quantitation, and was consistent with the upper limits of

the recommended dilution range to be suggested in the interlaboratory protocol sent to each participant (see Section 3.1 and Appendix I). Corresponding numbers and types of bottles filled with deionized water served as controls. In those cases where effects of citric acid were evaluated, the deionized water used was heat-sterilized to prevent any stimulation of microbial activity by the citrate, a potential bacterial nutrient.

All test containers and solution contents were maintained in the dark at ambient temperature (ca. 22° C) during the entire study. Small aliquots of each test solution were periodically taken by an adjustable pipet with a disposable polypropylene tip for total tin determination by GFAA. At each sampling time corresponding samples of control bottle and $SnCl_2$ test bottle solutions were also compared with a freshly prepared external tin standard ($SnCl_2$) solution. All periodic analyses were conducted in replicate (5 determinations) and the means ± standard deviations of single measurements were plotted against time (Figures 1 and 2).

2.3.1 Selection of Container Material and Solvent for the Tributyltin Research Material.

The effects of container materials on tin solution stability are presented graphically in Figure 1. Although some loss of solution strength is evident for all container materials, the loss seen for a tributyltin solution stored in a polyethylene bottle is the most dramatic. This finding illustrates the unsuitability of polyethylene materials for use in trace level organotin work. Experience in our laboratory with pyrex glass and polycarbonate materials indicates that either is

acceptable for use as organotin solution or environmental sample container. An additional solution stability experiment was conducted with polyethylene bottles to determine if the adsorbent effect of the polyethylene could be moderated by addition of 0.01M citric acid to the tin solutions. Figure 2 shows that the citric acid added to the tin solutions did prevent the rapid adsorption of tributyltin by polyethylene.

2.4 Chromatographic Preparation of Aqueous Tri-n-Butyltin Solution

The speciated, aqueous tributyltin research sample distributed for the organotin measurement methods intercomparison was prepared using the apparatus described below and illustrated in Figure 3. The entire research sample was made in a single 12 liter batch to insure sample homogeneity. A generator column technique was used to produce a saturated aqueous solution of tributyltin which was immediately diluted on-line to prevent precipitation. The generator column consisted of a 6 mm OD Pyrex tube joined to a short section of 9 mm Pyrex tubing. The overall column was 40 cm in length, the column bed was 25 cm in length and entirely enclosed in a water jacket for temperature control. Water jacket temperature was controlled by connection to a constant temperature bath. Generator column temperature (approx. 15°C) was maintained sufficiently below ambient (20-22°C) to insure that no tributyltin species would precipitate from solution upon elution from the generator column. The column packing, Chromosorb W HP 100/120 mesh, (Supelco, Inc., Bellfonte, PA 16823) was retained in the column by silanized glass wool plugs.

A pair of large 13-liter Pyrex glass bottles were employed as deionized water reservoir and final organotin solution receiving vessel, respectively.

The solution in each bottle was stirred with teflon covered stirring bars and purged with high purity nitrogen continuously from before organotin solution generation began until the sample was subdivided into 125 mL bottles for final storage and distribution. A stainless steel duplex LC pump (Model 2396, LDC/Milton-Roy Co., Rivera Beach, FL 33404) pumped source water through the generator column and to a 'T' fitting located at the eluent end of the chromatographic generator column. With the exception of the stainless steel components in the pump head, the wetted surfaces of the sample preparation apparatus were composed exclusively of borosilicate glass (Pyrex) or teflon. Since the bis(tributyltin)oxide (TBTO) used to load the generator column was introduced to the system downstream of the LC pump, the organotin-containing effluent came into contact only with glass or teflon surfaces, always under a nitrogen atmosphere. This anaerobic exposure to container materials was maintained throughout the entire process of analyte generation. Nitrogen purging of the receiving vessel continued until all the 125 mL sample bottles were filled. No attempt was made to fill the 125 mL sample bottles under controlled atmosphere conditions, they were filled and sealed in laboratory air.

2.4.1 Chromatographic and Sample Bottling Procedure

With the LC pump off, approx. 100 microliters of neat redistilled bis(tributyltin)oxide was added to the top of the generator column using an all-glass syringe and a teflon needle. Deionized water flow at 0.5 mL per minute was then started through the generator column, and an equal separate flow was delivered to the 'T' fitting just downstream of the column. Tin concentration in the effluent was periodically monitored by

graphite furnace atomic absorption (GFAA) to establish dilution ratios and column performance. When the tin concentration in the column effluent reached equilibrium, typically after 2-3 hours, the effluent was collected in the solution receiving bottle. When GFAA monitoring of the effluent indicated a drop in tin concentration, usually after 18 to 20 hours, the generator column was reloaded with TBTO, the column reequilibrated, and the solution once again collected in the solution receiving reservoir.

The complete tri-n-butyltin batch solution so prepared was subdivided in two decanting sessions into new 125 mL borosilicate glass bottles secured with teflon-lined caps. Prior to filling, the bottles were rinsed with methanol, then acid leached as described above, and dried in a laboratory oven. After filling with tri-n-butyltin solution, each bottle was immediately capped with a teflon lined screw cap and wrapped in parafilm M sealer and, to exclude light, aluminum foil. The order of filling sample bottles was noted for future reference by sequential numbering of each bottle as it was filled then wrapped. All sample bottles so prepared were maintained at ambient conditions, 22-25 °C, 40-60% R.H. during and since, excepting those shipped to participants.

2.4.2 Distribution of the Tri-n-Butyltin Samples and Follow-up Studies

Following communication with proposed laboratories and verification of their acceptance of the proposed intercomparison protocol (see Appendix I), each participant was mailed a single bottle of the tributyltin research material as prepared above. Bottles were selected randomly, since the entire lot of numbered bottles had been remixed and blindly drawn for mailing by a non-technical staff member. The actual sample identity

numbers were recorded for each participant laboratory. Since the total number of samples prepared in the lot taken for this study exceeded the number needed for participants, the Protocol (Appendix I) provided accommodation to any participant requiring additional samples owing to non-receipt or loss in the laboratory. In addition, the excess samples so prepared permitted subsequent archival studies during and since the round-robin completion. This has included random sacrifice of greater than 10% of the remaining population to critically evaluate shelf stability or modes of decomposition induced by analytical procedures, as suggested by participants subsequent to their contributions. Several of these highly significant findings are described in Section 3.0, with recommendations for new work.

3.0 Results and Discussion

3.1 Protocol Used and Level and Character of Participation

Appendix I provides a facsimile of the initial contact letter, response form, and details concerning each participants elected method(s) of total and/or molecular tin analysis. Another section of the Protocol illustrated in Appendix I details the uniform dilution scheme recommended for each participating organization, and approximate sample concentration range (expressed as total tin in µg/L) for guidance in instrumental settings, and the preferred means to report numerical results for statistical analysis at NBS. Specific information regarding the expected shelf-life of the aqueous tributyltin samples, directions for obtaining replicate samples in the event of misfortune, and the stringent means

exercised by the NBS for maintaining anonymity of each participant's results, while yet providing a summary of the entire range of variability by method or any preparation history was also provided. All the participating laboratories (35 in total) cooperated expeditiously and fully, with only several delays incurred by mailing or laboratory losses.

Table 1 lists some of the analytical methods currently available for organotin determinations. Table 2 lists the participants by country, with no identifying reference to their methods or submitted results. It can be clearly seen from the distribution of nationality and type of organization that an excellent response was obtained in this inaugural intercomparison. Not only are contributors from tin-producing and using nations well represented, so also are analytical experts representing academic, governmental, and industrial laboratories.

3.2 Statistical Analysis of Results

Aliquot samples of an aqueous tributyltin solution, nominally at a concentration of 1 µg/mL (1 ppm) were sent to nearly 50 laboratories. Thirty-five sets of results from 32 tin samples were returned to NBS. As discussed elsewhere in this report, the aliquot samples were believed to contain only the tributyltin species. The analytical results from several of the laboratories that undertook speciation analysis, however, have shown other tin species. We believe these additional species may be produced by the analytical procedures and are not representative of the aliquot solution, as discussed below.

To avoid questions regarding the expression of analytical data, we have converted the concentrations of all reported tin species to a total tin concentration. The converted total tin data for the 35 sets of reported

results are listed in Table 3. An inspection of these data shows that 3 of the sets of results (marked by asterisks) are very different from the results of the remaining 32. The average results from these 3 laboratories are 0.03, 2.4, and 6.0 ppm tin. The extreme values of the averages from all the remaining determinations are 0.30 and 1.6 ppm tin. The three results (marked by asterisks) were judged to be outliers, and are not used further.

Each cooperating laboratory used its own method of analysis. We have grouped the methods into 7 general categories (A-G), and have made a preliminary statistical analysis on these groups. A general description of the 7 groups is given in Table 4. The average tin values for the 7 groups and the standard deviations of these averages are summarized in Table 5. The averages are not significantly different from the nominal aliquot solution value of 1 ppm tin. In general, there does not appear to be any consistent biases between the 7 groups.

The combined results for the 32 laboratories with acceptable tin determinations are rather remarkable for a methods intercomparison that placed no constraint on the method employed for sample analysis. A frequency diagram (histogram) of the laboratory results is shown in Figure 4. The analytical methods A-G are indicated in the figure. The results tend to be distributed rather evenly about the central 1 ppm point, the approximate true value of tin in the research sample. The histogram shows an almost uniform distribution of analysis methods throughout the range of concentrations reported, with a very narrow peak at the center. A more detailed examination of the analytical methods comprising the narrow center peak of 20 laboratory results shows a rather uniform distribution of methods within the peak itself.

Since all of the different methods of analysis give very similar results, we have chosen to ignore the analytical groupings in the remaining statistical evaluations. A one-way analysis of variance (37,38) was used to determine the within- and between-laboratory components of variance. The square roots of these components of variance are called the within- and between-laboratory components of standard deviation, and are 0.08 and 0.28 ppm tin, respectively. The within-laboratory imprecision of 0.08 ppm tin is small relative to the between-laboratory imprecision. This is a common situation in interlaboratory studies. The overall average total tin value from all laboratory results (excluding the 3 outlier results) is 1.00 ± 0.05 ppm. The ± uncertainty is one standard deviation of the average. The measurement method that we have chosen as the benchmark method for determination of the true concentration of total tin in the research material is neutron activation analysis (NAA). We feel it is the least likely, of the methods available, to be subject to inaccuracies produced by methodology or sample matrix interference. The total tin value measured at NBS by neutron activation analysis for the research sample is 1.06 ± 0.05 μg/g (ppm). The relative standard deviation of the NAA analysis is 4.4 percent. The NAA procedure is described in Appendix II.

Because of the very unusual non-Gaussian distribution of laboratory results from this study, we refrain from making general probability statements. The interlaboratory results have been described by the histogram and by the components of standard deviation. Based on our experience with interlaboratory methods comparisons, it is believed that these interlaboratory results are generally quite good.

3.3.2 Problems Reported by Participants Concerning Samples Provided

Most laboratories chose to determine the total tin content of the research sample rather than to attempt speciation of the molecular moiety in solution. Two reporting participants claimed that their analysis for tin in molecular form(s) indicated that the original aqueous tri-n-butyltin research material either contained impurity monobutyl- and dibutyl-tin species, or that the sample underwent decomposition during transit and/or storage. These concerns are understandably very significant because in addition to authenticating sample shelf life, another NBS concern was to assess whether any or some of the various analytical methods employed by the participants might actually induce redistribution of the original tributyltin moiety, possibly occurring in stepwise manner (11,40), viz.,

$$2Bu_3Sn^+ \text{ ---------> } Bu_2Sn^{2+} + Bu_4Sn \qquad (1)$$

$$2Bu_2Sn^{2+} \text{ ---------> } BuSn^{3+} + Bu_3Sn^+ \qquad (2)$$

Most analytical methods cited in the literature (Table 1), affording chemical speciation of such an organotin mixture suggested by equations 1 and 2, do not provide for analysis of the neutral, often volatile tetra-organotins. Recognizing this need, we have recently extended previous work employing speciation analysis of aquatic methyl and butyltins (22,36) to a comprehensive scheme for determination of the complete butyltin series shown here plus likely methylbutyltin mixed species such as

recently reported by others (19). This method utilizes a novel combination of simultaneous extraction-derivatization by methylene chloride-sodium borohydride from water followed by direct injection into a gas chromatograph coupled with a highly sensitive tin-selective flame photometric detector (GC-FPD), described above in Section 2.2.2.

Applying the improved simultaneous extraction-hydridization method with GC-FPD, we have sacrificed nearly 10% of the original tributyltin sample stock, selected randomly, in order to assess whether changes had occurred in stored bottles. In addition to this, we also exposed some bottles to both conventional laboratory mercury vapor fluorescent lights and direct sunlight on a South-facing office window sill. To some of the sample bottles were added small (100 ppm) amounts of acetone, representing both expected concentrations frequently reported in forming dilute aqueous solutions of organotins from concentrated organic solutions, and typical C_1 photosenitizers encountered in environmental media (41,42). Regular stock samples kept in darkness served as controls.

Figure 5 depicts a series of GC-FPD analyses, clearly showing that a random selection of the NBS sample stock stored for nearly 5 months, about the midpoint during which participant laboratories were analyzing their samples, consisted entirely (> 99%) of the aquated tri-n-butyltin cation. On the other hand, long exposure to direct sunlight (through both window and Pyrex glass) and laboratory fluorescent light caused decomposition of the initial Bu_3Sn^+ moiety in some bottles, probably by Sn-C bond scission only rather than redistribution (equation 1) since no tetra-butyltin was detected (Table 6). After 5 months storage, two bottles received acetone spikes (100 ppm final concentration), one was stored in sunlight (number 261) and

one in darkness (number 265). The dark sample did not show acetone-stimulated decomposition of Bu_3Sn^+ after an additional years' storage (Table 6). However, exposure of the acetone spiked test bottle to sunlight for 4 months resulted in decomposition at a more rapid pace. Here di- (4.5% of the total butyltins), mono- (1.0%) and tetrabutyltin (1.0%) species were present, suggesting that pathways described by equations 1 and 2 are operative.

Samples analyzed after 17 months storage (Table 6) in the dark underwent only very slight degradation to dibutyltin (ca. 1%). Mass balances for total tin in the dark-stored bottles gave virtually identical values ($x = 1.10$, $s = 0.04$ ppm) to the NAA values for total tin.

In sum, dark-stored bottles remain extremely stable in terms of total tin and Bu_3Sn^+ values. Extended storage under fluorescent light or sunlight resulted in enhanced degradation of tributyltin to other butyltin species in certain bottles.

We conclude from these results that, while some participants reported that appreciable "impurity butyltins" or "decomposition" occurred in the NBS-supplied samples, we have seen no evidence to persuade us that this is the case. Rather, we feel all analytical methodology, especially that requiring vigorous extraction/derivatization must be carefully examined for subtle stoichiometric or catalytic effects - often photoinitiated - which might induce disproportionation and decomposition reactions at Sn-C bonds. At NBS, we have been so far unable to detect such alterations in any of the dark-stored round-robin samples retained and sacrificed at 5 month and 17 month periods for such archival studies, as summarized in Table 6. For this methods intercomparison, no attempts were made to produce a sterile research

material. Viable microorganisms existed in all bottles tested after 5 months storage in the dark. Viable cell counts (on 1/4 strength nutrient agar, 3 days incubation, 22°C) ranged from 125 to 1195 cells per mL. The viable cells apparently had little, if any, influence on tributyltin speciation in these dark stored samples (Table 6).

3.4 Basic Chemistry of the Chromatographic Generator Column

Formation of pure, stable organotins solutions in water is a notoriously difficult procedure, subject to wide variations in products and non-reproducible behaviors. Much of the difficulty stems from the unfamiliar surfactant and lipophilic properties of organotin cations, strongly dependent upon the number and size of their carbofunctional groups (43). Notwithstanding their generally low solubilities in water (typically < 10 ppm), also dependent upon carbon number or size of covalently bound organic functions (18) the presence of easily dissociable geganions (anions) can importantly affect both solubilities and stabilities. In designing our production of large homogeneous batches of pure aquated tri-n-butyltin cation, we selected an approach derived from our successful applications of ion exchange chromatography (29). For ease of manipulation and prepurification of starting material we chose freshly redistilled, neat liquid bis-(tributyltin) oxide which could be directly injected onto a suitable chromatographic substrate. The LC column packing selected was an acid washed, silane treated diatomaceous material, chromosorb W HP of 100/120 mesh size. Consequently, an extensive highly reactive reaction bed containing both Si-O-Si and Si-OH or $Si-OH_2$ sites was provided for equilibration of saturated solutions of $Bu_3Sn-O-SnBu_3$ via surface

facilitated hydrolysis interactions, as summarized in Figure 6. Such a cyclic process can be readily maintained because of the great excess of water and active silica surface area over the Bu_3SnOH precursor TBTO, as the net reaction (Figure 6) reveals.

The induction periods required to produce a LC eluent with constant Bu_3Sn^+ concentration probably reflect rates of hydrolysis controlled chiefly by equations B and C in Figure 6.

In sum, the generator column approach to production of both small (mL) and large (>10 L) homogeneous batches of pure tri-n-butyltin cation in water has proven effective. Of special note is the likelihood that this chromatographic technique can, in principle (29), be applied to a rather large array of organotins precursors, both covalent as with liquid TBTO, and solid ionic compounds such as aryltin halides, for example. Principal limitations will involve rates of hydrolysis on the reaction flow (column) bed (equations B, C, Figure 6), flow rates required to generate sufficient quantities, and the final concentrations to be prepared for each organotin moiety.

5.0 Conclusions

One of the more important findings drawn from this inaugural organotin measurement methods intercomparison is that a low concentration (ca. 1 ppm) aqueous organotin research material could be produced with the stability and chemical purity necessary for a material upon which a methods intercomparison could be based. Prior to the production and subsequent monitoring of the research material used in this study, the long term fate, in terms of

concentration and chemical species fidelity, of a low concentration organotin solution was unknown.

The analysis of analytical data generated during this measurement methods intercomparison demonstrates that any one of the 7 different methods employed by the participants in this intercomparison can yield accurate total tin measurement values. The distribution of results does not indicate a bias inherent in any specific method, but only laboratory to laboratory variation in the accuracy of total tin determination.

Since this methods intercomparison was initiated, several laboratories have reported improvements in the detection levels for state-of-art tin determinations by up to three orders of magnitude. This improved sensitivity now allows detection of organotin compounds at environmental action level concentrations (ca. ng/L levels) for individual organotin species. It is therefore clear that a definitive methods intercomparison, designed to evaluate organotin speciation methodology by use of a multi-species organotin research material, is both desirable and feasible. Moreover, in view of increasing international concern with the environmental fate and effect of organotins, an evaluation of organotin speciation methods is necessary. Because of the orders of magnitude differences in toxicity between the individual butyltin compounds, qualified speciation data is an absolute requirement for accurate assessment of the environmental effects of organotins and determination of the persistence. Manufacturers may also find application for certified speciation data in areas of product specification and quality control.

An absolute calibration of the major organotin biocide, tributyltin, and its known primary degradation product, dibutyltin, is essential to

insure that all laboratory and field data are fully supported by calibrated analyses. This need cannot be met with total tin determinations of a single species organotin research material. Production of a multi-species organotin research material with a fixed ratio of di- to tributyltin would be responsive to real world environmental issues and the measurement needs of monitoring and regulatory agencies. Based on input from the first organotin methods intercomparison participants and the limited published speciation data available at environmental concentrations, a ratio of 2:1 or greater (Bu_3Sn:Bu_2Sn), at an overall total tin concentration of 200 to 500 ppb, would appear to be an appropriate reflection of field measurement experience. A research material of this type would provide users with a useful standard for dilution into either natural saline or freshwater matricies using dilutions of ca. 10^4 to generate samples at environmental levels of 20 to 50 ng/L.

Production of a multi-species organotin research material will require NBS to additionally certify, by independent non-destructive means, the total tin concentration along with the individual species concentrations in the multi-species research material, thereby insuring total mass balance agreement in the solution. As mentioned above, a two species organotin research material is now considered timely and essential, but its generation raises critical questions concerning the shelf-life and resistance to degradation by redistribution of the dual-species solution.

Concern about biologically induced redistribution, fortuitously shown to be no problem in the initial, non-sterile intercomparison sample, must be reduced by synthesis of a sterile multi-species organotin research material. Prior to distribution, the multi-species solution would need to be monitored

for a suitable period of time (60 to 90 days) to insure there is no sample redistribution by chemical, catalytic or enzymatic processes exceeding an acceptable level of approximately 1%.

The foregoing research has established the basis for transition of measurement methodology developed in the research laboratory to qualified procedures available to users in the manufacturing and monitoring fields. The measurement methods intercomparison study now concluded makes clear the feasibility of a more sophisticated speciation methods intercomparison addressing international concerns of organotin use. We recommend that effort be directed to the synthesis of a multi-species organotin research material for use in marine, freshwater, or biotic media.

6.0 Acknowledgments

In conclusion, we would like to thank all the laboratories that responded to our inquiry as to interest in an organotin measurement methods intercomparison. Special thanks go to all laboratories that invested time and resources to make tin determinations of the first intercomparison sample and return data to NBS. We also thank Cheryl Matthias and Greg Olson for monitoring the stability of the intercomparison samples.

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UNITED STATES DEPARTMENT OF COMMERCE
National Bureau of Standards
Washington, D.C. 20234

October 5, 1983

The National Bureau of Standards is conducting an interlaboratory comparison of analytical methods for the measurement of organotin compounds in aqueous solution. This work is supported in part by the U.S. Office of Naval Research (ONR) and is concerned with establishing the variance between different organotin measurement methods and providing the basis for ultimately generating organotin standard reference materials (SRM) involving relevant environmental matrices such as sea water, sediment, or tissue. The initial sample will be a tri-n-butyltin compound in deionized water. Tributyltin is an organotin species with world-wide importance in terms of commercial usage and analytical interest.

Because of your well-known interest in organotin compounds, we invite your participation in the methods intercomparison. A reply form is included in the enclosure, which we request that you return as soon as possible, whether you plan to participate in the intercomparison or not. As noted in the enclosure, the identity of the participating laboratories will be kept confidential. We also invite your use of this sample for comparison of two or more methods of tin analyses within your laboratory, i.e., an established speciation method and a new, preliminary method or a total tin versus a speciated tin method.

Your comments and suggestions concerning this methods intercomparison are welcomed, please feel free to write me, or telephone (301) 921-2849. We hope to begin distribution of samples by late October/early November, 1983. We hope to include your laboratory among those participating in the intercomparison.

Sincerely,

William R. Blair

William R. Blair
Chemical & Biodegradation Processes Group
Inorganic Materials Division
Rm. A329/Bldg. 223
National Bureau of Standards
Washington, DC 20234 U.S.A.

Enclosure

Interlaboratory Comparison of Measurement Methods
for Trace Organotin Compounds in Water

OBJECTIVES

A series of aqueous organotin solutions are being prepared at the National Bureau of Standards (NBS) for use in an interlaboratory comparison of total and/or organotin measurement methods. NBS has been asked by the U.S. Office of Naval Research (ONR) to provide samples and coordinate data tabulation as part of an ongoing NBS program investigating the environmental fate and effect of organotins. Considerable interest in the intercomparison has been expressed by laboratories conducting organotin research around the world. Consequently, we decided to invite par-- ticipation by all interested laboratories, with more than 20 participants expected.

Initially, a tributyltin-x compound in deionized water will be distributed for analysis by the method(s) currently in use at each laboratory. Ultimately, a similar sample using a sea water and possibly a sediment matrix will also be provided for analysis. It is hoped that this inaugural intercomparison will indicate the variance of current analysis methods, resulting in identification or development of an internationally recognized standard analytical method(s) for the determination and speciation of organotins in aquatic media.

SAMPLE PREPARATION AT NBS

The tributyltin-x samples will be supplied in new clear borosilicate glass bottles with Teflon-lined caps. A comparison between glass and polycarbonate container materials is contemplated, but initial samples will be supplied in glass bottles only. Prior to use, the bottles will be rinsed with an organic solvent (methanol) to remove manufacturing residues, then leached for 15 to 18 hours with aqueous 10 percent HNO_3 at 40 °C to remove any trace metal contamination. The tributyltin-x solution will be prepared in a single batch of six to eight liters by on-line dilution of a saturated, aqueous, solution of tributyltin-x delivered through a thermostated chromatographic column (1-3). The preparation, storage, and dispensing of the tributyltin-x solution will be done under an N_2 atmosphere. A sufficient number of samples will be prepared so that in case of loss or damage to a sample during shipping, a maximum of one duplicate can be provided. Control samples, maintained at NBS, will be stored both under normal laboratory lighting conditions and in the dark. The total tin concentration of the sample will be stated only as a nominal value to prevent overload of analytical instrument detectors. Anticipated sample size is 100 mL, with a total tin concentration in the low part-per-million (µg/mL) range.

INDIVIDUAL LABORATORY PARTICIPATION

Your request to participate in the intercomparison of measurements will indicate agreement to report sample analysis within 30 days of receipt of the sample and to report the following information based on determination of either speciated tin or total tin or both:

(1) Values for eight replicate analyses of the sample. A replicate analysis is here defined as a separate aliquot taken individually for analysis from the original bottle containing the tin solution supplied by NBS. Do not send averages or standard deviation values, the eight individual measurements will be used to calculate averages and standard deviation values, and to evaluate bias and random errors in reported results.

(2) Concise description(s) of method(s) used for sample analysis.

Rather than try to provide several samples at different concentrations, only one sample will be provided. The concentration should be high enough to prevent significant losses during storage and shipping. Upon receipt, samples must be stored in the dark at a temperature of 20 to 22 °C. Prior to analysis the sample will need to be diluted to protect most tin-selective detectors. We recommend a dilution of at least 1000:1 to more realistically approximate environmental concentrations.

The identity of the individual laboratories participating in the intercomparison will be kept confidential, with each lab knowing only its own coded identity symbol.

COLLECTION OF DATA

Data collection, reduction, tabulation, and plotting will be handled by a statistical analysis group at NBS, with the results of the intercomparison being mailed to participants as soon as all data are reported and processed.

ANALYSIS OF RESULTS

The data received from each participant will be compiled into a table indicating the variance between methods. The concentration of tin in the sample will be determined at NBS by neutron activation analysis. This value will be supplied with the results mailed to each participant so the accuracy of the method used may be determined.

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INTERLABORATORY ORGANOTIN SPECIATION STUDY
PARTICIPANT INFORMATION

Please complete and return this sheet as soon as possible to:

Mr. William R. Blair
Rm. A331/Bldg. 223 (Materials)
National Bureau of Standards
Washington, DC 20234 USA
Tel. (301) 921-2849

☐ We wish to participate in the organotin interlaboratory comparison.

☐ We do not wish to participate.

Signed: _____

For those participating:

(1) We will submit analytical data to Mr. William R. Blair within _____ weeks (fill in blank) of receiving the sample.

(2) We will measure
☐ speciated tin
☐ total tin
☐ both of the above

(3) Summary (1 to 2 sentences) of analytical method(s) to be used for measurement(s) specified in (2) above:

(Give literature reference if appropriate.)

(4) Name and address for shipment of sample:

(5) Name and address (if different from 4) for person(s) conducting analysis.

Appendix II

Report of Analysis of Tributlytin Solutions for Total Tin Content by Neutron Activation Analysis

D. A. Becker
Inorganic Analytical Research Division
Center for Analytical Chemistry

Four samples were received in tightly capped, foil covered bottles with the numbers 174, 214, 254, and 262. Samples were analyzed as received.

Procedure: After several gentle inversions of the bottle, sample solutions were poured directly into precleaned, weighed 2 dram polyethylene vials, which were again weighed to determine sample weight. Vials were then immediately sealed with a hot soldering iron, packaged as required in the irradiation capsule, and immediately irradiated in the NBS Reactor (NBSR) for analysis.

Standards were made from NBS SRM 1057b, Dibutyltin bis (2-ethylhexanoate). After drying, a standard solution of this matrial in paraffin oil was made, having a concentration of 335.9 µg Sn/g oil. For working standards, a weighed amount of the stock solution was diluted with pure paraffin oil inside of the 2 dram vial used for that irradiation. Amounts of tin in each standard ranged from approximately 30-90 µg.

Samples and standards were each analyzed individually according to the following procedure: irradiation for 2 minutes in the RT-3 pneumatic tube facility of the NBSR (neutron flux is 4.9×10^{13} n/cm^2s); decay time

of 9 minutes during which the samples (standards) in the 2 dram vials were mixed by repeated inversion and positioned on a high resolution germanium semi-conductor detector; samples were then counted for 1200 seconds clock time, and the 332 key peak of Sn-125 m (Ti/2 = 9.52 m) was used for the determination of total tin.

Results and Discussion: Results of this analysis are shown in Table 1. All four bottles were analyzed at least once, and two were analyzed in duplicate. Agreement is good, providing a total tin concentration in the sample solutions of 1.06 ± 0.05 µg/g. The relative standard deviation (1s) of the analysis was 4.4 percent.

It should be noted that a separate evaluation of the possible matrix effects due to differing hydrogen content of water versus paraffin oil was made, and showed no detectable effect. Also, both samples and standards were irradiated and counted in the horizontal position, which effectively eliminated errors due to geometry differences from differing sample sizes. Blank values for the clean polyethylene vials plus pure paraffin oil were found to be negligible. In addition, the agreement between data values obtained on 16-17 May and on 21 August may indicate that these solutions as delivered are stable over this period of time.

Table 1 for Appendix II

Table 1. Results from Tin Analysis

Bottle Number	Sample Weight (g)	Tin Concentration (µg/g)
174	7.3611	1.09
174[a]	5.7468	1.06
214	7.2932	1.07
254	7.7043	0.99
262	7.4438	1.02
262[a]	5.9272	1.12
	MEAN	1.06
	STD.DEV.(1s;n-1)	0.047
	STD.DEV.(relative)	4.4 percent

[a] These samples were analyzed on 21 August 1984. All others were analyzed on 16-17 May, 1984.

TABLE 1

SOME SPECIATION METHODS IN CURRENT USE FOR ORGANOTINS

(Substrate(s)) Derivatization, Preconcentration	Separation Scheme	Detector(s) Employed	Tin Species; Method Detn. Limits, µg/mL	Refs
DIRECT SOLVENT EXTRACTION				
(B) benzene, reflux	none	NMR,XRF,GFAA	Oct_2Sn; 40	1
(T) HCl + hexane	GC	H-FID	R_4Sn (R=Et, Pr,Bu); 100	2
(T) R_4NOH + toluene	none	GFAA	total organic inorg. Sn	11
(M) MeOH + HCl	MeOH/hexane on alumina	GFAA	Bu_nSn, n=2,3; < 0.2	12
DIRECT HYDRIDIZATION				
(M) sparge w/ or w/o $NaBH_4$ on Tenax-GC	GC	FPD	Me_nSn, n=0-4; 0.013-0.053 Bu_nSn, n=1,2; 0.018-0.037, n=1,2; PhSn; 0.023	3
(T) direct sparge w/ homogenate	GC	MS	Me_nSn, n=1-4; > 1 ng/g	10
EXTRACTION WITH HYDRIDIZATION				
(W) $CHCl_2$ extr, $LiAlH_4$/hexane	GC	EC,FID	Ph_nSn, n=1-4; 3-15	4
EXTRACTION WITH ALKYLATION				
(W) benzene/tropolone extr + BuMgBr	GC	FAA	Me_nSn, n=0-3; 0.04 w/5 L water	5
(W) benzene/tropolone extr + PeMgBr	GC	FPD	Bu_nSn, n=0-3; 0.060-0.150	6
COMPLEXOMETRIC/SPECTROPHOTOMETRIC				
(W) 3,4-dithiol satd polyurethane	LC w/NaOH + acetone	UV at 650 nm	Sn(IV); 0.04	7
(M) silica gel w/ MeOH-HOAc	TLC w/ hexane-HOAc	GFAA of spots	R_nSn, n=1-3; air, 0.1 µg/m^3 waters, 100 µg/L soils, 1 µg/g	8
MISCELLANEOUS				
(W) direct injection	cation exchange HPLC	GFAA	R_nSn, n=1,2 R=alkyl, aryl; 25-150	9

NOTES FOR TABLE 1

Matrix speciated: (B) = beverage; (W) = natural waters; (T) = tissues; (M) = mixed matrices, air, water, sediments, dusts.

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TABLE 2

COUNTRY	INSTITUTE	ADDRESS	NAME
Canada	National Water Research Institute Environmental Contaminants Division	867 Lakeshore Road Burlington, Ontario L7R 4A6	Dr. Y.K. Chau Dr. G.A. Bengert
Canada	NWRI-ECD Department of Environment Canada Centre for Inland Waters	867 Lakeshore Road Burlington, Ontario L7R 4A6	Dr. R.J. Maguire
France	Centre Oceanologique De Bretagne	Service Geochimie D3GM B.P. 337 29273 Brest Cedex	Dr. J.L. Charlou
France	I.N.S.C.I.R.	B.P. 08 76130 Mont Saint Aignan	Melle Devaud
France	Institut Francais de Recherche pout L'Exploitation de La Mer (IFREMer)	B.P. 1049 44037 Nantes Cedex	Dr. C. Alzieu
France	Universite De Pau et Des Pays De L'Addur Laboratorie De Chemie Analytique Faculte De Sciences	Avenue L. Sallenave 64000 Pau	Dr. Prof. M. Astruc Dr. R. Pinel
France	S.N.E.A.(P) Centre Micoulau	Avenue du President Angot 64018 pau Cedex	M.M. Guillerme and Sirvins
Great Britain	International Paint Marine Laboratory	Yealm Road; Newton Ferrers Plymouth Devon	Dr. P.D. Tyson
Great Britain	International Tin Research Institute Chemistry Division	Fraser Road, Perivale Greenford, Middlesex UB6 7AQ	Dr. P.J. Smith Dr. A.H. Chapman
Great Britain	M.A.F.F. Fisheries Laboratory	Rememberance Avenue Bernham-on-Crouch Essex	Dr. M. I. Waldock
Italy	Instituto per la Corrosione Marina dei Metalli C.N.R.	Via Mercanzia 4 16123 Genova	Dr. Prof. E. Mor

TABLE 2 (CONTINUED)

Japan	Department of Hygiene and Preventive Medicine Faculty of Medicine	University of Tokyo 7-3-1, Hongo, Bunkyo-ku Tokyo 113	Dr. Y. Arakawa
Japan	Nitto Kasei Co., Ltd.	3-17-14 Nishiawaji 3-Chome Higashiyodogawa-Ku	Dr. T. Tsutsui Dr. T. Hamachi
Japan	Nippon Oil and Fats Co., Ltd. Mikuni Factory, Technical Division	No. 15-51, 4 Chome, Niitaka Yodogawa-ku, Osaka	Dr. H. Doi
Norway	A/S Jotungruppen Analytical Lab	P.O. Box 400 N-3201 Sandefjord	Dr. P. Rosmanith
Switzerland	Institut Fur Toxikologie	Schorenstr. 16 CH-8603 Schwerzenbach	Dr. P. Schmid
Switzerland	Swiss Federal Research Station for Fruit Growing, Viticulture and Horticulture	CH-8820 Waedenswil	Dr. M.D. Muller
USA	Chesapeake Biological Lab.	P.O. Box 38 Solomons, Maryland 20688	Dr. J.C. Means
USA	David W. Taylor Naval Ship Research and Development Center Code 2830 Code 2841	Annapolis, Maryland 21402	Mr. P. Schatzberg Mr. H.S. Preiser
USA	Florida State University Department of Oceanography	Tallahassee, Florida 32306	Dr. M.O. Andreae Mr. J.T. Byrd
USA	Johns Hopkins University Applied Physics Laboratory Aquatic Ecology Section	Shady Side, Maryland 20764	Dr. L.W. Hall Jr. Dr. M. Lenkevich
USA	Kinnetic Laboratories, Inc.	P.O. Box 1040 3050 Paul Sweet Road Santa Cruz, California 95061	Dr. A.B. Thum
USA	M & T Chemicals	P.O. Box 1104 Rahway, New Jersey 08540	Dr. A.E. Slesinger Mr. I. Simmons

TABLE 2 (CONTINUED)

USA	North Carolina Department of Natural Resources and Community Development	P.O. Box 27687 Raleigh, North Carolina 27611-7687	Dr. R.E. Kelling
USA	Naval Ocean Systems Center Code 521	San Diego, CA 92152	Dr. P. F. Seligman
West Germany	CIBA-GEIGY Marienberg GMBH Analytical Chemistry	Postfach Z09 D-6140 Bensheim 1	Dr. H. Muller
West Germany	Institutl fur Geowissenschaften Johannes Gutenberg Universitat	Saar Str. 21 Postfach 3980 D-6500 Mainz	Dr. Prof. H. J. Tobschall Dr. U. Oehmichen

TABLE 3

LABORATORY RESULTS OF TIN DETERMINATIONS
GROUPED BY METHOD OF ANALYSIS (A-G) VALUES IN PPM TOTAL TIN

ARBITRARY LAB NUMBER	METHOD A			METHOD C				METHOD D		
	1	2	3	18*	19	20	21	22	23	24
	.41	1.37	1.17	0.027	1.098	1.07	1.14	1.099	1.00	0.65
		1.21	1.40	0.028	1.127	1.07	1.11	0.974	1.11	0.61
		1.35	1.11	0.028	1.147	0.94	0.95	1.081	1.05	0.69
		1.21	1.18	0.028	1.113	1.07	1.00	0.921		
		1.28	1.14	0.028	1.113	0.94	0.99	0.960		
		1.32	1.31	0.028	1.015	1.09	1.06	1.027		
		1.30	1.08	0.027	1.029		1.01	0.966		
		1.28	1.09	0.027	1.078		1.09	0.891		

METHOD B												
4*	5	6	7	8	9	10	11	12	13	14	15	16
6.3	1.61	1.10	1.00	0.98	1.128	1.048	0.75	1.067	0.59	1.13	0.281	0.90
6.1	1.76	0.86	1.00	0.94	1.138	0.968	0.85	1.076	0.59	0.98	0.257	1.00
5.9	1.55	0.91	1.10	0.98	1.208	0.998	0.90	1.080	0.58	1.04	0.286	1.04
5.9	1.68	0.81	1.00	0.94	1.288	0.918	0.90	1.087	0.57	1.08	0.292	1.08
5.9	-	1.01	1.10	0.98	1.208	0.888	0.90	1.099	0.56	1.08	0.314	1.00
5.9	-	0.86	1.00	0.94	1.308	1.068	0.90	1.099	0.51		0.269	1.04
5.8	-	0.81	1.00	0.98	1.258	1.188	1.00	1.080			0.358	
6.0	-	0.86	1.10	0.94	1.328	1.108	1.00	1.056			0.316	
							1.10					

METHOD E					METHOD F		METHOD G			
25*	26	27	28	29	30	31	32	33	34	35
2.11	1.40	0.821	0.96	1.83	0.94	0.93	1.04	0.78	0.908	0.96
2.55	1.20	0.840	0.99	1.80	0.98	0.91	0.93	0.81	0.765	1.04
2.40	1.10	0.781	0.91	1.69	1.02	0.96			1.075	1.14
2.55	1.50	0.755	0.91	1.43	1.11	0.89			0.908	0.92
2.64	1.40	0.759	0.97	1.46	1.07	0.92			0.908	0.96
2.32	1.70	0.818	0.82	1.61	0.98	0.97			1.023	
2.44	1.50	0.880	0.93	1.47	1.02	0.93			0.975	
2.78	1.40	0.766	0.99	1.54	1.02	0.96			0.918	
									0.975	
									0.975	
									0.980	
									0.985	
									0.980	
									0.961	
									0.980	

* Values not used in statistical analysis of results

TABLE 4

MEASUREMENT METHOD CATEGORIES

Method Category	Extractant	Derivitization	Separation	Detector
A	None	None or $KMnO_4$, H_2SO_4	None	graphite furnace atomic absorption (GFAA)
B	MIBK cyclohexane toluene dichloromethane with tropolone and HCl or HBr	None	None	GFAA
C	None or acetic acid	Hydride	None or Thermal desorption	Quartz furnace atomic absorption
D	benzene with tropolone or hexane with acetic acid	MeMgCl or bomb digestion	None or gas chromatography	Quartz furnace or nonspecified atomic absorption
E	benzene pentane dichloromethane hexane some with tropolone and HCl or HBr	Hydride or Grignard	Thermal desorption or gas chromatography	flame photometric
F	cyclohexane hexane with HCl	None	Thermal desorption or gas chromatography	electron capture detector
G	chloroform dichloromethane	dithiol or Grignard or H_2O_2/H_2SO_4	None or gas chromatography	colorometric mass spectrometer

TABLE 5

Analytical Method Averages and Standard Deviations

Method	Total Tin mg/L (ppm) Average	Std. Dev. from the Average	Number of Laboratories
A	0.962	0.277	3
B	0.974	0.087	13
C	1.055	0.018	3
D	0.898	0.125	3
E	1.185	0.189	4
F	0.976	0.042	2
G	0.935	0.048	4

TABLE 6

STABILITY OF ORGANOTIN RESEARCH MATERIAL
Analysis after 5 months of storage

Bottle #	Storage Condition	% organotin species detected; nd = not detected			
		$BuSn^{+++}$	Bu_2Sn^{++}	Bu_3Sn^{+}	Bu_4Sn
177	lab light[1]	trace	1.0	99	nd
206	lab light	nd	0.6	99.4	nd
261	sunlight[2]	nd	1.2	98.8	nd
267	sunlight	0.8	4.4	94.8	nd
152	dark	nd	0.7	99.3	nd
162	dark	nd	nd	100	nd
258	dark	nd	nd	100	nd
265	dark	nd	nd	100	nd
167	dark	nd	nd	100	nd

	Analysis after 17 months of storage, conditions as above				GFAA TOTAL TIN
177	3.4	4.0	92.6	nd	1.55
206	nd	0.9	99.1	nd	1.43
261*	----------	not speciated		----------	1.14
267	----------	not speciated		----------	0.87
152	nd	2.5	97.5	nd	1.12
162	nd	0.7	99.3	nd	1.15
258	nd	0.4	99.6	nd	1.05
265*	nd	0.7	99.3	nd	1.05
167	nd	1.6	98.4	nd	1.13

[1] Laboratory fluorescent lights
[2] Sunlight coming through south facing office window and pyrex sample bottle
* Samples receiving 100 ppm addition of acetone, after analysis of 5 months of storage. Bottle 261 after 9 months contained 93.5% Bu_3Sn^{+}, 4.5% Bu_2Sn^{2+}, 1% each of $BuSn^{3+}$, Bu_4Sn.

Figure Captions

Figure 1. The effect of different container materials on the short term 48 hour) stability of aqueous inorganic and tributyltin solutions with an initial concentration of 30 ppb (30 µg/L). A dramatic loss of solution strength is seen with the tributyltin solution stored in a polyethylene container, demonstrating the unsuitability of polyethylene for storage of organotin reference solutions or samples containing organotin compounds.

Figure 2. Addition of 0.01 M citric acid to 30 ppb (30 µg/L) aqueous solutions of inorganic and tributyltin stored in polyethylene containers results in stabilization of the solutions, presumably by reducing adsorption losses to the container walls.

Figure 3. Schematic diagram of the chromatographic generator column apparatus used for synthesis of the tributyltin research material distributed during this methods intercomparison.

Figure 4. Frequency diagram of the results of analysis of the tributyltin research material by intercomparison participants. The total number of participants was 32. The analytical methods used (A to G), are located above a concentration scale indicating the distribution of values determined. The results tend to be evenly distributed about the center (1.0 ppm) point.

Figure 5. Analysis by GC-FPD of the contents of some of the intercomparison samples retained at NBS and opened after 137 days of dark storage at 22°C. Nine bottles altogether were opened and analyzed and all gave virtually identical results. Sample 267 was analyzed with spikes of mono-, di-, and tetrabutyltin species at levels which would represent 6% degradation of the tributyltin to each particular species (top chromatogram).

Figure 6. Schematic representation of the reactions occurring on the generator column during tributyltin solution synthesis.

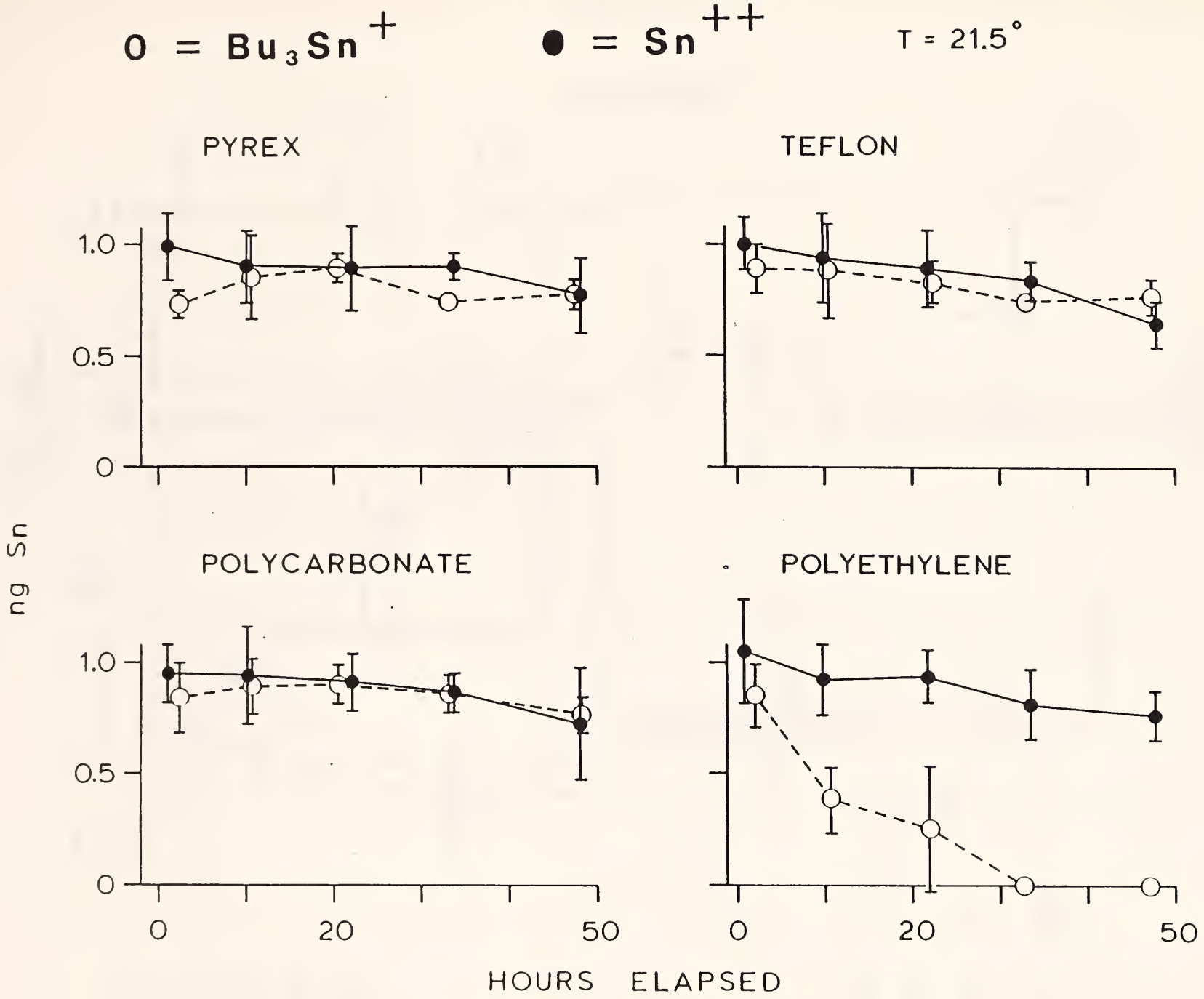

O = Bu3Sn+
● = Sn++
T = 21.5°
PYREX
TEFLON
POLYCARBONATE
POLYETHYLENE
ng Sn
1.0
0.5
0
0
20
50
HOURS ELAPSED

Figure 1

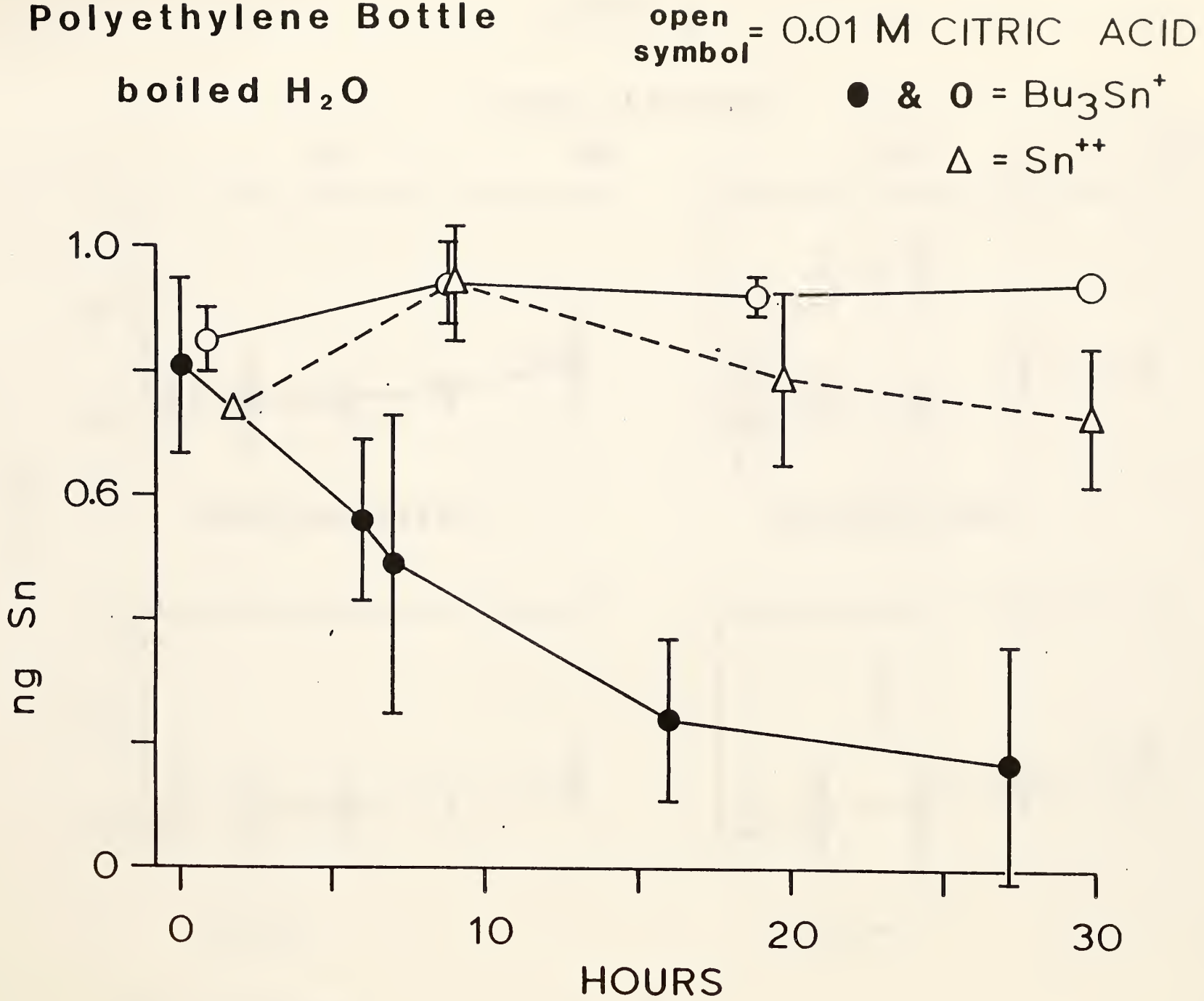

Polyethylene Bottle
boiled H_2O
open symbol = 0.01 M CITRIC ACID
● & O = Bu_3Sn^+
Δ = Sn^{++}
1.0
0.6
0
ng Sn
0
10
20
30
HOURS

Figure 2

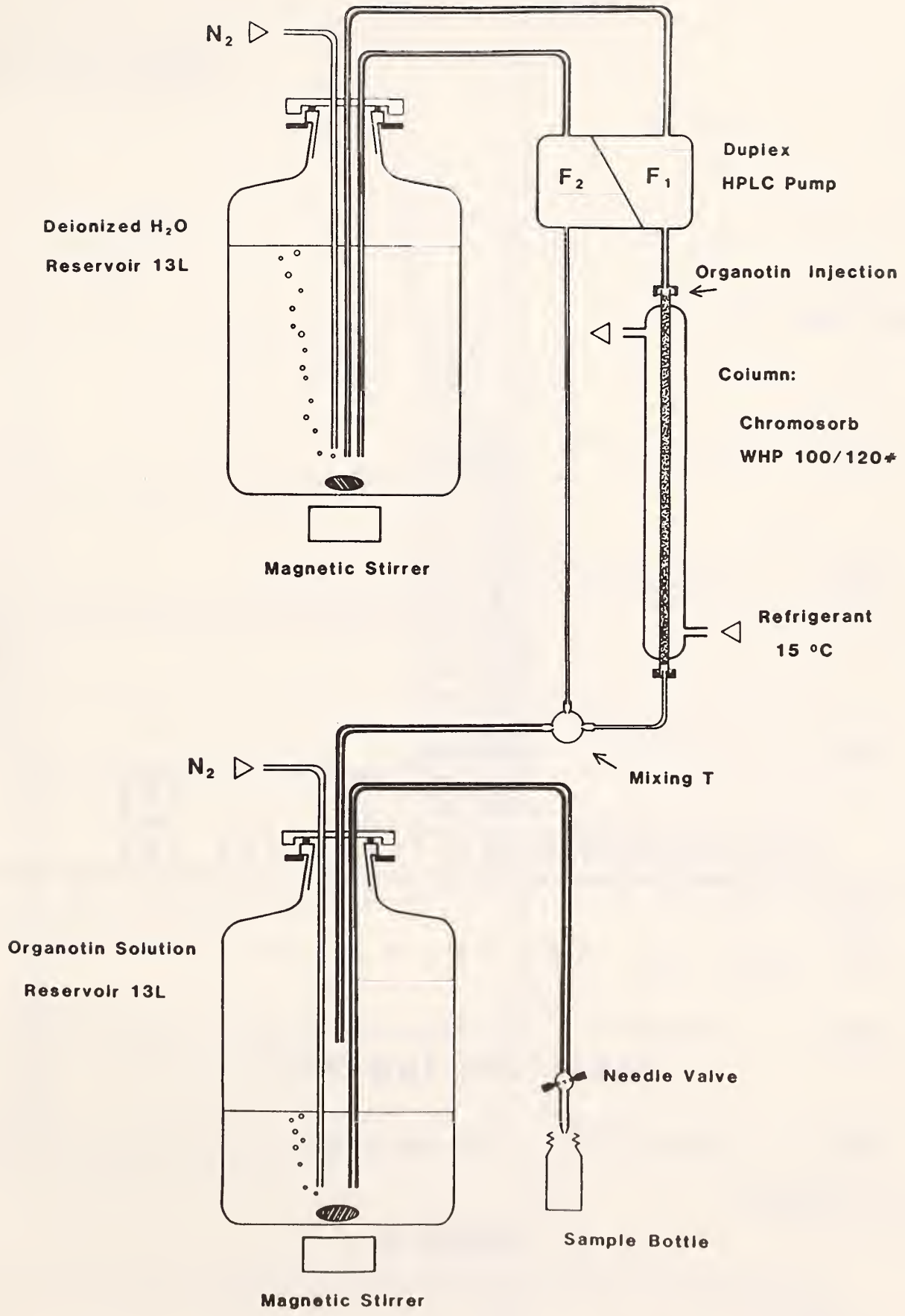

N_2
Deionized H_2O
Reservoir 13L
Magnetic Stirrer
F_2
F_1
Duplex
HPLC Pump
Organotin Injection
Column:
Chromosorb
WHP 100/120#
Refrigerant
15 °C
Mixing T
N_2
Organotin Solution
Reservoir 13L
Needle Valve
Sample Bottle
Magnetic Stirrer

Figure 3

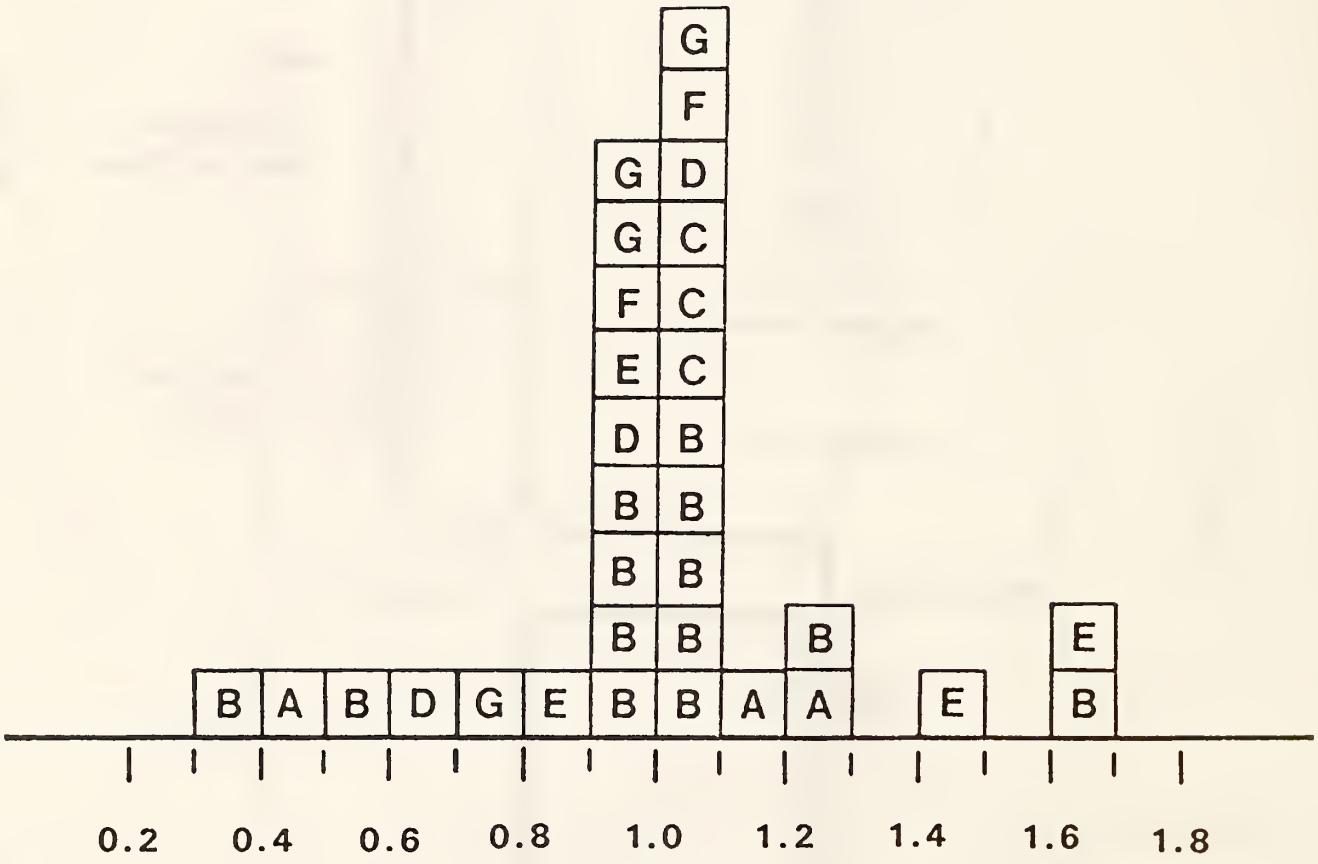

G
F
G D
G C
F C
E C
D B
B B
B B
B B B E
B A B D G E B B A A E B
0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8
Total Tin (µg/mL)

Figure 4

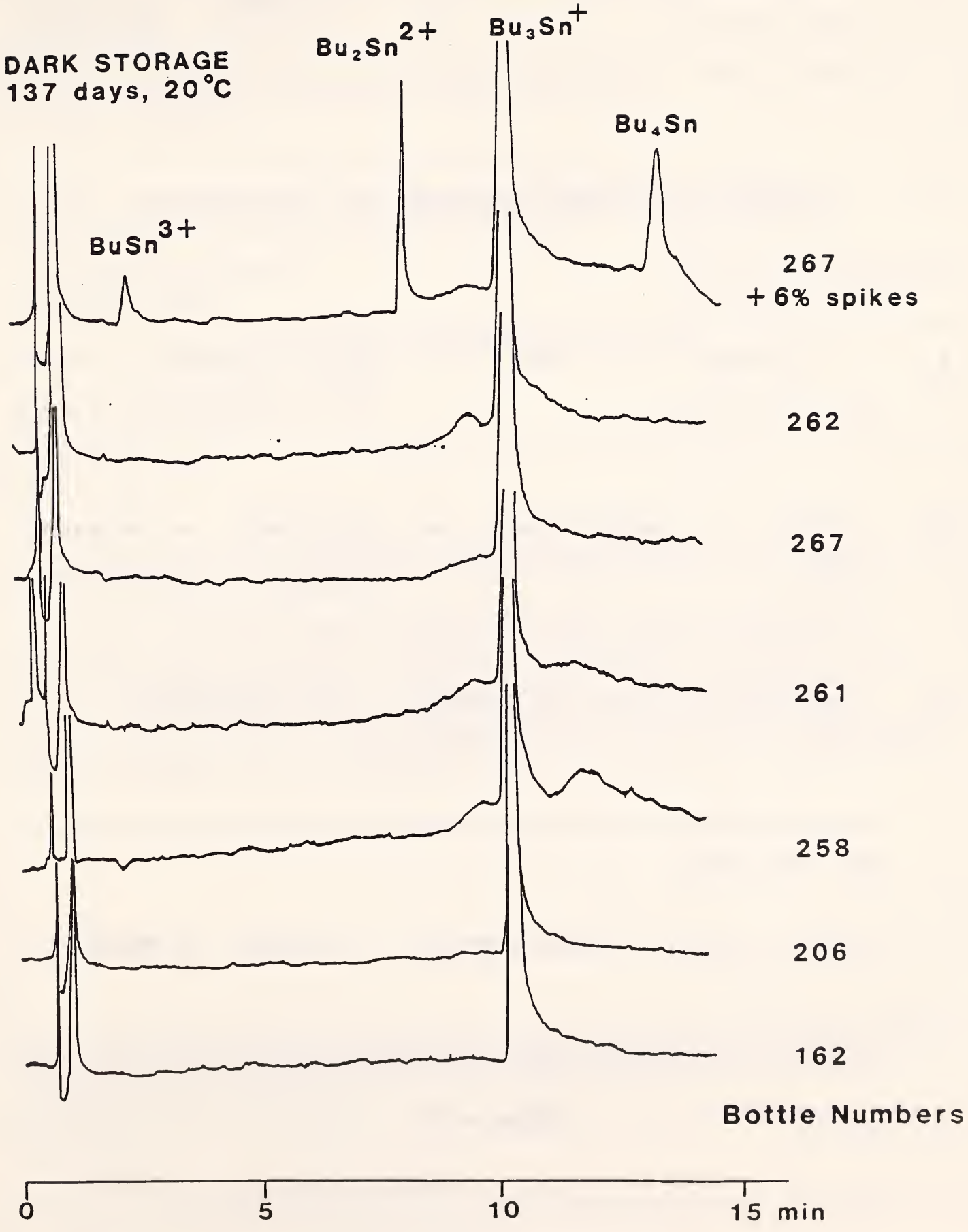
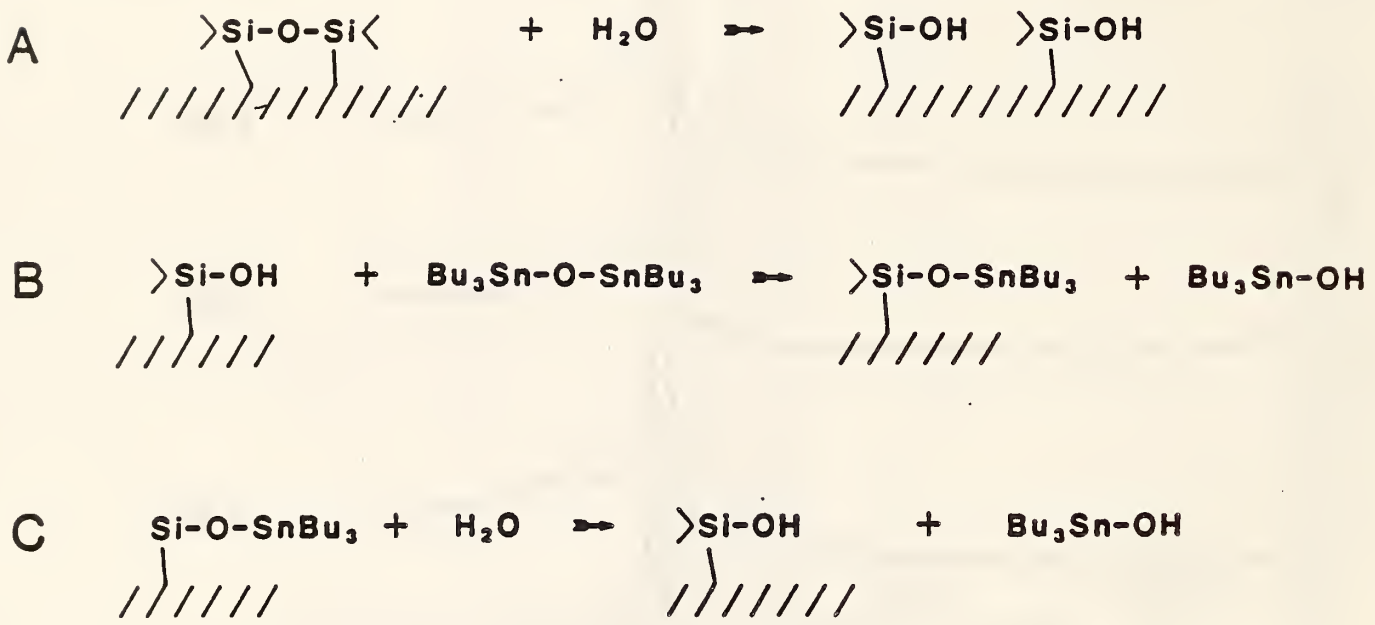

DARK STORAGE
137 days, 20°C
Bu_2Sn^{2+}
Bu_3Sn^{+}
Bu_4Sn
$BuSn^{3+}$
267
+6% spikes
262
267
261
258
206
162
Bottle Numbers
0
5
10
15 min

Figure 5

GENERATOR COLUMN SYNTHESIS OF ORGANOTINS



NET REACTION:

$$Si\text{-}O\text{-}Si + 2H_2O + Bu_3Sn\text{-}O\text{-}SnBu_3 \rightarrow 2\,Si\text{-}OH + 2\,Bu_3Sn\text{-}OH$$

Figure 6

NBS-114A (REV. 2-80)

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11. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)

A comparison of prevalent organotin measurement methods has been conducted on an international scale with a new tri-n-butyltin research material distributed to over 40 participating laboratories worldwide. A description of background research into the behavior and manipulation of low-concentration (ppm) aqueous organotin solutions, chromatographic production and packaging of the stable speciated butyltin research material in water, and quantitative results from the international methods intercomparison are reported here along with recommendations for future work.

12. KEY WORDS (Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)

Chemical speciation; Liquid chromatography; Methods intercomparison; Molecular characterization; Research material; Round-robin; Stability; Tributyltin; Organotin solutions.

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